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## (54) HEAT-SHRINKABLE ETHYLENE POLYMER FILMS

(71) We, E. I. DU PONT DE NEMOURS AND COMPANY, a Corporation organised and existing under the Laws of the State of Delaware, located at Wilmington, State of Delaware, United States of America, do hereby declare the invention for which we pray that a Patent may be granted to us and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention relates to heat-shrinkable ethylene polymer films, their production, and to polymer blends useful for producing such films.

Heat-shrinkable films prepared from ethylene polymers have gained acceptance in a wide variety of packaging applications, due in part to the clarity of such films and their ability to form a tight package at relatively low shrink temperatures. These films are often prepared by tubular extrusion processes from blends of high and low density polymers.

Unfortunately, the preparation of such films at thicknesses of less than one mil by these techniques has been less than completely successful. Specifically, it has heretofore not been possible to prepare an ethylene polymer film at efficient production rates having high clarity and shrink force and a thickness of less than one mil. Further, the shrink force of films previously available has limited their use in certain applications where an exceptionally high force is required.

The present invention relates to a unique blend of ethylene polymers which can be used for the efficient preparation of thin, heat-shrinkable films by conventional melt extrusion techniques.

Specifically, the invention provides a polymer blend having an ultimate elongation of at least 700% at 120° C. and consisting essentially of a substantially homogeneous mixture of

(1) from 70% to 80% by weight, based on the total weight of the blend, of a low density polymer selected from (a) polyethylene and (b) copolymers of ethylene and from 1% to 6% by weight of vinyl acetate, the polymer having a density of from 0.91 to 0.93 gram/cc. at 25° C., a melt index of from 1.5 to 12.0 and a melting point of from 95° C to 110° C.,

(2) from 30% to 20% by weight of a high density copolymer of ethylene with at least one alpha olefin of 3 to 12 carbon atoms, the high density copolymer having a density of from 0.94 to 0.98 gram/cc at 25° C., a melt index of from 0.2 to 1.5, a stress exponent of at least 1.5, and an ultimate elongation of at least 1400% at 120° C.

The present invention also provides a process for the preparation of heat-shrinkable film by melt extrusion of the above blend into a self-supporting sheet at a melt temperature of from 190 to 225° C followed by orienting the extruded film through stretching the unoriented sheet in two mutually perpendicular directions in the plane of the sheet to at least 3 times the original dimension of the sheet in each direction at a temperature of from 90° to 120° C., and thereafter cooling the sheet while maintaining its stretched dimensions.

There is further provided a heat-shrinkable film resulting from the above process characterized by a percent shrinkage of at least 20% along each axis of the plane of the sheet at a temperature of 100° C., a haze value of less than 3.0, a gloss value of greater than 100 and a transparency value of at least 60.

The present invention is based on the discovery of a unique combination of polymer

composition, ultimate elongation, and other polymer characteristics which permit the preparation of exceptionally good heat shrinkable films having a thickness of less than 1.0 mil which can be efficiently prepared at commercially acceptable production rates. The above characteristics have been found to be dependent on the method of preparation of the components of the blend.

As indicated, the low density component of the polymer blend can be either an ethylene homopolymer or a copolymer of ethylene with from 1 to 6% vinyl acetate. The low density polymer can have a density of from 0.91 to 0.93 and a melting point of from 95° to 110° C. The melt index of resins which can be used in the invention can vary over a substantially greater range than had previously been thought possible, and values of from 1.5 to 12.0 are used in the invention. Exceptionally good extrusion characteristics are obtained with a low density resin having a density of from 0.910 to 0.925 gram/cc. at 25° C., and a melt index of from 1.5 to 3.0.

The high density component can be a copolymer of ethylene with at least one alpha olefin having from 3 to 12 carbon atoms including, for example, propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-decene and 1-dodecene. Of these, ethylene/1-decene and ethylene/1-octene copolymers are particularly preferred. In a preferred embodiment of the invention, the high density component of the blend has a density of from 0.940 to 0.965 gram/cc. at 25° C., a melt index of from 0.4 to 1.0 and a process exponent of at least 1.7. In an especially preferred embodiment, the alpha olefin is 1-octene comprising from 0.5 to 1.0% by weight of the copolymer.

The low density polymer preferably is prepared according to the autoclave process. The autoclave process, in accordance with the instant invention, is understood to include those methods of polymer preparation in which cold monomer, with or without initiator, is passed directly into a hot polymerization mixture is maintained at a substantially constant temperature. The autoclave process is to be contrasted with the tubular method of preparation wherein the monomer mixture containing initiator is passed through a preheater which heats the mixture to a temperature range in which polymerization begins and the subsequent increase in temperature of the mixture is a function of the liberation of heat by the polymerization reaction. In the tubular process, the subsequent rise in temperature is controlled by removal of the heat from the exterior of the reaction vessel, for example, by coolant in the surrounding jacket. Thus, a basic distinction between the autoclave and tubular methods of preparation is that in the autoclave process, the maximum conversion is determined by the temperature differential between the

incoming monomer and the reaction mixture, while the conversion in a tubular process, by contrast, is primarily determined by the temperature differential between the initiation temperature and the peak temperature to which the reaction mixture is permitted to attain by external control.

Particular apparatus arrangements which can be used for the preparation of low density polymers according to the autoclave process are described, for example, in United States Patent 2,897,183.

The high density component of the resin blend, in accordance with the instant invention, has an ultimate elongation of at least 900% at 120° C. as measured on a compression molded sample. It has been found that this degree of ultimate elongation is necessary for the extrudability of the resin blend into thin films at commercially acceptable rates of production. The ultimate elongation can be determined on a tensile testing machine such as that commercially available as Model TT-B from Instron Engineering Company of Quincy, Massachusetts (Instron is a trade mark). The high density component of the blend is tested by compression molding a 25 mil thick sheet at a temperature of 180° C. and a pressure of 500 psi, and cooling the sheet to room temperature in the press. The test specimen, die cut from this sheet, has a thickness of 25 mils, a nominal gauge length of 0.15 inch and a nominal minimal width of 0.125 inch. The edges of the specimen are semicircular, with the concave side out, having a radius of 0.075 inch. The specimen geometry, with a crosshead separation speed of 5 inches per minute, provides a nominal strain rate of 330% per minute.

The high density resins may be prepared by a continuous two-step process involving an initial polymerization of monomer in a tubular reaction zone and continuously passing the reaction mixture directly into a constant environment autoclave reactor to complete the synthesis, and thereafter separating the resulting polymer. This process is fully described in British Specification No. 1,051,183.

These high density resins, themselves blends of high and low molecular weight polymers, can also be formulated through the separate preparation and subsequent blending of polymers of molecular weights corresponding to those synthesized in the stages of the process described in British Specification No. 1,051,183. The blending can be effected, for example, by simultaneous melt extrusion of the high and low molecular weight polymers under intensive shearing conditions such as in a Banbury mixer.

The low and high density polymer resins, having been separately prepared are blended in the relative proportions indicated by any conventional blending techniques which will produce a substantially uniform, homogeneous

blend. In general, additives such as slip agents, antioxidants and the like, for further modification of the performance characteristics of the resulting films, are added in the course of the blending operation prior to extrusion.

In accordance with the present invention, the blend of polymers has an ultimate elongation of at least 700%. The ultimate elongation of the resin blend is measured on an extruded strip specimen. The specimen is extruded as a 16 mil thick strip drawn down from a 50 mil die opening through a one inch air gap directly into water. The temperature of the blend at the die is 200° C. and the strip is extruded at a rate of 14 lbs./hr./in. of die width. The elongation of the extruded strip can then be measured on an Instron tensile testing machine in accordance with the procedure used for determination of the ultimate elongation of molded specimens of the high density component of the resin blend.

The blend can be melt extruded into a film in either flat or tubular form by extrusion processes conventionally used in the production of thermoplastic polymeric film, and thereafter biaxially oriented by stretching in each of two mutually perpendicular directions. A particularly useful process and apparatus for the extrusion and orientation of films of this type is the tubular process and apparatus described in British Specification No. 921,308.

The films are biaxially oriented by stretching at least 3× in each direction, at a temperature of from 90° to 120° C. Exceptionally good heat-shrink characteristics are obtained when the films are stretched at least 5× in each direction at a temperature of from 105° to 120° C.

The unique resin blends and the process of the instant invention permit the preparation of heat-shrinkable films at god production rates which exhibit product characteristics equal to or better than heat-shrinkable polyethylene films previously available to the art. In addition, for the first time, the instant invention enables the production of films having a thickness of less than one mil using tubular extrusion methods at commercially acceptable rates of production efficiency.

The interplay of the several required parameters for the resin blend and the contribution of each toward the ability to form exceptionally thin, high quality films is not fully understood. However, high pressure autoclave prepared low density resins of the specified compositions and physical characteristics are believed to have a narrower molecular weight distribution and are more Newtonian in rheological character than high pressure tubular prepared resins. Resins prepared according to the high pressure autoclave process are characterized by relatively high critical shear rate. Values of 3000<sup>-1</sup> seconds or higher

are observed in typical resin formulations. These factors are believed to be primary considerations in the excellent drawn-down characteristics observed for the resin blends of the instant invention.

In the high density resin component of the blend, it is believed that the high molecular weight fraction synthesized in the tubular portion of the process in British Specification No. 1,051,183 has an important and desirable influence on the elongation versus temperature characteristics of the final blends.

The heat-shrinkable films of this invention have excellent optical properties which permit effective display of articles packaged in the heat-shrinkable film in addition to having good shrinkage characteristics and high shrink force which causes the film to shrink tightly around irregular objects to provide well-conformed, skin-tight packages. The films of the invention exhibit marked improvements in shrink characteristics over films made from ethylene polymer blends previously thought to give optimum performance.

Still further, the films of this invention show excellent durability characteristics at low temperature, which is desirable since skin-tight packaging is being employed to an increasing extent in the wrapping of food-stuffs such as poultry, meats, and various meats which are held in refrigerated storage or in frozen conditions for long periods of time. These films have good clarity, a feature which is most valuable for effective display of articles in shrink packages; they can be readily heat-sealed to give packages free of unsightly puckering at the seal; and, because of their good surface properties, they can be used more efficiently on wrapping machines than present commercial films.

The films of the invention are useful in a wide variety of packaging applications, such as shrink covers for use on aluminum foil and molded pulp trays for baked goods. They are also useful in shrink tube packages wherein elongated articles such as window shades and shelf linings are rolled into small rolls and inserted into a sleeve of the tubing, the tubing sleeve is then heated to shrink the tubing, thus affording a very compact, readily handled package. Another type of package is the shrink sleeve package wherein elongated gated trays of vegetables such as celery or fruit, eggs and the like can be overwrapped with the sleeve, the sleeve then being shrunk in place, leaving the compact tight package with open ends for ventilation. Still another application is the packaging of fresh produce such as lettuce, broccoli, celery and the like in a wrapping of the film of this invention wherein the package is twisted and then heated slightly to shrink the package into a compact unit. Further applications include multi-packaging of cans, bottles, golf balls, light bulbs, electronic supplies such as

radio tubes, and in replacement of carton dividers, use as tray covers and as direct wraps on such products as bacon, frankfurters, fresh meat and fresh poultry. These films can also be used as wraps on processed meats and on such dairy products as cheese. They can also be used in the form of contour bags for wrapping of smoked meats, sausage products and frozen poultry. They can be used as shrink covers in baked goods, food containers, containers for metal parts such as hardware, for textiles, candy and the like, as shrink sleeves on cartons of household items such as spices, on cups, dishes, silverware, paint brushes, electrical core packs, combination packs of several different articles, on rolls of film, paper, metal foil, as tape strips for packaging small items such as washers, nuts, bolts, buttons, as bubble type display packages of cosmetics, small hardware, electronic parts and household items.

In the following Examples, which further illustrate the invention, parts and percentages are by weight. The following tests are used in the evaluation of the several resin blends and the resulting films.

Melt Index (MI) is determined as described in ASTM-D-1238-65T; Condition E.

Stress exponent is calculated from the following formula:

$$\text{Stress exponent} = \frac{\log \frac{\text{flow rate at load 2}}{\text{flow rate at load 1}}}{\frac{\text{load 2}}{\text{load 1}}}$$

Flow rates are determined according to the method used in determining melt index (ASTM-D-1238) by measuring the amount of flow in 10 minutes at 190° C. under the specified load. For these determinations, load 2 is 6480 grams and load 1 is 2160 grams.

Density is determined by preparing the sample as described in ASTM-D-1248-60T and measuring its density as described in ASTM-D-1505-63T.

Shrinkage is determined by measuring a given area of the film, dipping the film in boiling water at 100° C. for 30 seconds, noting the change in dimension and calculating percent shrinkage, based on the original dimension.

Transparency is determined as described in ASTM-D-1746-62T.

20° Gloss is determined as described in ASTM-D-2457-65T.

Haze is determined as described in ASTM-D-1003-61.

Melting point is determined with a Du Pont Model 900 Differential Thermal Analyzer. The sample is heated to above 150° C., cooled to room temperature, and then reheated at 15° C./min.

Production efficiency is a percentage determination based on the amount of time that a given extrusion apparatus yields acceptable product.

The ultimate elongations of the high density components and the resin blends are respectively measured according to the procedures previously described.

In all of the Examples, the low density and high density resin components are thoroughly blended and, in addition to the specific resins, are all further blended with 200 parts per million of 2,6 - di - t - butyl - 4 - methylphenol antioxidant, approximately 120 parts oleamide, 48 parts of stearamide, and 500 parts per million of silica. The blends are then melt extruded at a temperature of 200° C. into a cast tube approximately 20 mils thick, using a 35 mill die opening. The films are then biaxially oriented at a temperature of 115° C. by stretching 5.8× in the MD and 5× in the TD directions. The process and apparatus used are substantially the same as that described in British Specification No. 921,308.

#### Example 1

Three resin blends were prepared, their characteristics are given in Table I. Resin "A" illustrates a resin of this invention while resin blends "B" and "C" are comparative control samples. Resin blend "B" is substantially the same as that illustrated in Example 1 of United States Patent 3,299,194.

Oriented films were prepared from the three resins and were evaluated. The results are summarized in Table II. Resin "A" was found to be superior to Resins "B" and "C" in its extrudability into thin gauge films. Film from Resin "A" excelled in optical properties and shrink characteristics.

#### Example 2

A resin blend having the composition of Resin "A" in Example 1 above was extruded and oriented to give a film having a final thickness of 1.5 mil. The film was prepared at a 72% production efficiency, and exhibited a transparency of 53% and a 20° gloss value of 146%.

TABLE I  
Resin Characterization

Characteristics		Resin		
		A	B	C
5	Low Density Component	74%	75%	75%
	Density	.924	.914	.915
	Melt Index	2.0	1.2	1.2
	Type	EVA	EH	EH
	High Density Component	26%	25%	25%
10	Density	.949	.954	.944
	Melt Index	.45	1.4	1.3
	Stress Exponent	1.85	1.3	1.3
	Ultimate Elongation %—120° C. (compression molded sample)	1850	450	680
15	Type	E/O	EH	E/B
	Low Density/High Density Polymer Blend			
	Density	.932	.925	.924
	Melt Index	1.2	0.9	.7
20	Ultimate Elongation %—120° C. (16 mil water quenched strip)	860	—	230
Legend: EH—Ethylene Homopolymer E/B—Ethylene/1-Butene Copolymer E/O—Ethylene/1-Octene Copolymer EVA—Ethylene/Vinyl Acetate (5%) Copolymer (M.P. 102° C. by Differential Thermal Analysis)				
25				

TABLE II  
Film Extrusion Results

		Resin		
		A	B	C
30	Oriented Film			
	Production Efficiency			
	0.6 mil	70—80	0	0
	0.75 mil	70—85	0	0
35	1.0 mil	70—85	40—50	40—50
	Oriented Film Properties			
	Total Haze, %			
	0.6 mil	2.1	—	—
	0.75 mil	2.4	—	—
40	1.0 mil	2.5	4	2.2
	20° Gloss, %			
	0.6 mil	150	—	—
	0.75 mil	145	—	—
	1.0 mil	130	95	115
45	Transparency, %			
	0.6 mil	71	—	—
	0.75 mil	61	—	—
	1.0 mil	53	55	55
	Shrinkage, % (1 Mil)			
50	M.D.	35	22	24
	T.D.	36	34	34
	Total	71	56	58

### Example 3

A resin blend was prepared having 73% polyethylene resin having a density of 0.916 gram/cc. at 25° C., a melt index of 4.0

and melting point of 106° C.; and 27% of ethylene/1-octene copolymer having a melt index of 0.45, a density of 0.949 gram/cc. at 25° C. and a stress exponent of 1.85. A 60

16 mil extruded strip from the blend had an elongation of 900% at 120° C. A cast film of the blended resins was extruded to produce a 0.75 mil thick film having a total shrinkage of 50% at 100° C., a haze value of 1.9%, a gloss value of 125% and transparency value of 61%. Oriented film production efficiency at the 0.75 mil thickness was 77.6%.

#### Example 4

A resin blend was prepared similar to resin blend "A" in Example 1, except that the low density component contained 3% by weight of vinyl acetate, had a melt index of 3.0 and a melting point of 104° C. A 16 mil extruded strip from the blend had an elongation of 860% at 120° C. The blend was formed into a 0.75 mil film having a total shrinkage of 49%, a haze value of 2.2%, a gloss value of 125% and a transparency value of 62%. Oriented film production efficiency was 77.0%.

#### WHAT WE CLAIM IS:—

1. A polymer blend having an ultimate elongation of at least 700% at 120° C. and consisting essentially of a substantially homogeneous mixture of

(1) from 70% to 80% by weight, based on the total weight of the blend, of a low density polymer selected from (a) polyethylene and (b) copolymers of ethylene and from 1% to 6% by weight of vinyl acetate, the polymer having a density of from 0.91 to 0.93 gram/cc. at 25° C., a melt index of from 1.5 to 12.0 and a melting point of from 95° C. to 110° C., and

(2) from 30% to 20% by weight of a high density copolymer of ethylene with at least one alpha olefin of 3 to 12 carbon atoms, the high density copolymer having a density of from 0.94 to 0.98 gram/cc. at 25° C., a melt index of from 0.2 to 1.5, a stress exponent of at least 1.5 and an ultimate elongation of at least 1400% at 120° C.

2. A polymer blend according to Claim 1 wherein the low density polymer has a density of from 0.910 to 0.925 gram/cc. at 25° C.

3. A polymer blend according to Claim 1 or 2 wherein the low density polymer has a melt index of from 1.5 to 3.0.

4. A polymer blend according to any of Claims 1 to 3 wherein the high density copolymer has a density of from 0.940 to 0.965 gram/cc. at 25° C.

5. A polymer blend according to any of Claims 1 to 4 wherein the high density copolymer has a melt index of from 0.4 to 1.0 and a stress exponent of at least 1.7.

6. A polymer blend according to any of Claims 1 to 5 wherein the high density copolymer consists essentially of ethylene/1-butene copolymer, ethylene/1-octene copolymer, or ethylene/1-decene copolymer.

7. A polymer blend according to Claim 6 wherein the high density copolymer component consists essentially of ethylene/1-octene copolymer comprising 1-octene units in an amount of from 0.5 to 1.0% based on the weight of the high density copolymer.

8. A process for preparing a heat-shrinkable sheet structure which comprises the sequential steps of melt extruding into a self-supporting sheet at a melt temperature of from 190° C. to 225° C. a substantially homogeneous blend according to any of Claims 1 to 7 and thereafter stretching the sheet in each of two mutually perpendicular directions in the plane of the sheet to at least 3 times the original dimension of the sheet at a temperature of from 90° C. to 120° C. and thereafter cooling the sheet while maintaining its stretched dimensions.

9. A process according to Claim 8 wherein the sheet is a self-supporting film.

10. A process according to Claim 9 wherein the film is stretched at least 5 times the original dimension of the film in each direction.

11. A process according to Claim 9 or 10 wherein the film is oriented at a temperature of from 105° C. to 120° C.

12. A process according to any of Claims 9 to 11 wherein the film is extruded and oriented by a tubular process.

13. A process according to any of Claims 9 to 12 wherein the film is extruded and oriented to a thickness of less than 1.0 mil (.0025 cm.).

14. A biaxially oriented heat-shrinkable film prepared by a process according to any of Claims 9 to 13, which film is characterized by a percent shrinkage of at least 20% along each axis in the plane of the sheet when subjected to a temperature of 100° C., a haze value of less than 3.0, a gloss value greater than 100 and a transparency value of at least 60.

15. A polymer blend according to claim 1 substantially as hereinbefore described with reference to any one of the Examples.

16. A biaxially oriented heat-shrinkable film according to claim 14 substantially as hereinbefore described with reference to any one of the Examples.

17. A process for preparing a heat-shrinkable film according to claim 8 substantially as hereinbefore described with reference to any one of the Examples.

5 18. Film whenever produced by the process of claim 17.

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